



(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 796 883 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:  
24.09.1997 Bulletin 1997/39

(51) Int. Cl.<sup>6</sup>: C08J 3/12, C08J 3/24,  
C08L 83/12

(21) Application number: 97104878.0

(22) Date of filing: 21.03.1997

(84) Designated Contracting States:  
DE FR GB IT

(30) Priority: 22.03.1996 JP 93287/96  
22.03.1996 JP 93288/96

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(54) Silicone rubber powder and preparation thereof

(57) There is disclosed a silicone rubber powder prepared from a curable silicone composition comprising a polyorganosiloxane having least one silicon-bonded polyoxyalkylene group of the formula



wherein R<sup>1</sup> is an alkylene radical, R<sup>2</sup> is an alkylene radical, R<sup>3</sup> is selected from hydrogen atom or alkyl radicals and m is an integer having a value of 2 to 100. The product rubber powder is preferably prepared by curing the above curable silicone composition to form a cured silicone rubber and by then pulverizing the product silicone rubber.

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**Description**

This invention provides a highly hydrophilic silicone rubber powder that has a soft feel, and also to the preparation thereof.

5      Silicone rubber powders are used as additives for cosmetics, paints, inks, and organic resins. Such powders are particularly well-suited for application as a cosmetic additive that provides a smooth feel or as a paint additive for deglossing paint films. These silicone rubber powders are generally exemplified by JP-A 59-68333; 64-56735; 64-70558; 64-81856; and 3-250050.

10     However, these silicone rubber powders have a poor flowability and hydrophilicity. As a result, when added to a waterborne cosmetic or paint, they either cannot be dispersed to homogeneity; or if a dispersion is obtained, the silicone rubber powder separates during storage. In response to these problems JP-A 7-102075 has proposed a silicone rubber powder having amorphous silica immobilized or anchored on the powder surface. Unfortunately, this powder itself has a rough, gritty feel and cosmetics formulated these with a rough, unnatural feel. Silicone rubber powders can also be prepared by emulsifying a curable silicone composition in an aqueous surfactant solution and thereafter curing 15     the composition. However, a poor hydrophilicity is still exhibited for the silicone rubber powders prepared from silicon-bonded polyoxyalkylene-functional polyorganosiloxane as a surfactant JP-A 4-183726.

An object of the present invention is to provide a highly hydrophilic silicone rubber powder that has a soft feel. Another object is to provide an efficient method for preparation of said powder.

20     The present invention, therefore, is a cured silicone rubber powder wherein at least one polyoxyalkylene group of the formula



25     is bonded to silicon in the polyorganosiloxane chains that form the rubber powder, where  $R^1$  and  $R^2$  are independently selected from alkylene,  $R^3$  is the hydrogen atom or alkyl, and  $m$  is an integer with a value of 2 to 100.

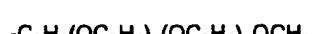
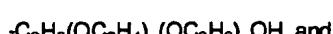
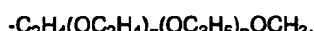
The preparative method of the present invention comprises pulverizing the above described silicone rubber.

30     The silicone rubber powder according to the present invention is characterized in that at least one polyoxyalkylene group of the formula



35     bonded to silicon in the polyorganosiloxane chains that form said powder.  $R^1$  is independently selected from alkylene radical having 1 to 20 carbon atoms, and is exemplified by ethylene, propylene, and butylene with ethylene or propylene being preferred.  $R^2$  is also independently selected from alkylene radical having 1 to 20 carbon atoms, which may be the same as or different from  $R^1$ . Ethylene is preferred for  $R^2$ .  $R^3$  is hydrogen atom or alkyl radical having 1 to 10 carbon atoms, and is exemplified by methyl, ethyl, and propyl. The subscript  $m$  in the formula is an integer with a value of 2 to 100, preferably 5 to 20. The molecular structure of this polyorganosiloxane is exemplified by straight-chain, partially branched straight-chain, branched-chain, cyclic, and resin structures with straight-chain or partially branched straight-chain structures being preferred.

40     The polyoxyalkylene group under consideration is exemplified by:



55     in which  $m$  is an integer with a value of 2 to 100,  $n$  is zero or a positive integer,  $p$  is a positive integer, and  $n + p$  is an

integer with a value of 2 to 100. Among these polyoxyalkylene groups, those whose main chain consists only of the (OC<sub>2</sub>H<sub>4</sub>) repeat unit are preferred for their ability to impart a soft feel and excellent hydrophilicity to the product silicone rubber powder. This subject polyoxyalkylene group must be bonded to a silicon atom in the polyorganosiloxane chains that form the silicone rubber.

5 The curing reaction that forms our silicone rubber is exemplified by the addition reaction between alkenyl and silicon-bonded hydrogen, the condensation reaction between silicon-bonded hydroxyl and silicon-bonded hydrogen, organoperoxide-induced radical reactions, and UV-induced radical reactions. The addition reaction system is particularly preferred. The introduction of the polyoxyalkylene group onto silicon in the polyorganosiloxane chains is realized by carrying out the curing reaction of the above reaction systems in the presence of a polyorganosiloxane whose silicon carries both the polyoxyalkylene group and a group that participates in the particular curing reaction. Similarly, the curing reaction in the above reaction systems is conducted in the presence of a polyoxyalkylene compound bearing a group that participates in the curing reaction. Alternatively, the silicon-bonded polyoxyalkylene-functional polyorganosiloxane is simply contained in the silicone rubber powder and does not participate in the curing reaction that produces silicone rubber.

10 15 Our silicone rubber powder has a JIS A durometer (JIS K 6301) preferably of 10 to 50, and more preferably of 20 to 45. The shape of our silicone rubber powder is exemplified by spherical, flattened or dish-like, and amorphous morphologies. It will have a spherical, flattened or disk-like shape when it is produced through spraying or emulsification. It will have an amorphous or irregular shape when it is produced by pulverization. The average particle size of the claimed silicone rubber powder is preferably no larger than 500 micrometers, and more preferably no larger than 250 micrometers.

20 25 The preparative method of the present invention is characterized by pulverizing a cured silicone rubber which is formed by curing a silicone composition of this invention. The technique for pulverizing a silicone rubber is exemplified by using a pulverizing or grinding device such as a stamp mill, bell crusher, roll mill, hammer mill, drum mill, and jet mill. Pulverization is preferably carried out while cooling with water or liquid nitrogen since pulverization can increase the temperature.

The corresponding addition reaction-curing silicone rubber composition preferably comprises

30 (A) 100 weight parts of a polyorganosiloxane that contains at least 2 silicon-bonded alkenyl groups in each molecule;

(B) a polyorganosiloxane containing at least 2 silicon-bonded hydrogen atoms in each molecule, in a quantity that provides 0.1 to 10 moles of silicon-bonded hydrogen from component (B) per one mole of alkenyl radical in the present composition;

(C) 0.001 to 20 weight parts of at least one polyoxyalkylene-containing component selected from

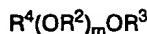
35 (i) an polyorganosiloxane that contains at least one polyoxyalkylene group of the formula



bonded to silicon,

40 or

(ii) a polyoxyalkylene compound of the formula



45 wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and m have their previously defined meanings and R<sup>4</sup> is alkenyl;

and

(D) a platinum catalyst in sufficient quantity to cure the composition.

50 Component (A) is a polyorganosiloxane that has at least 2 silicon-bonded alkenyl groups in each molecule. The molecular structure of component (A) is a straight-chain, partially branched straight-chain, branched-chain, cyclic, or resin structure, with straight-chain and partially branched straight-chain structures being preferred. The alkenyl groups of component (A) are vinyl, allyl, butenyl, pentenyl, and hexenyl with vinyl being preferred. The non-alkenyl silicon-bonded groups in component (A) are exemplified by hydroxyl; alkoxy, such as methoxy, ethoxy, and propoxy; and substituted or unsubstituted monovalent hydrocarbons. The substituted and unsubstituted monovalent hydrocarbons are alkyl, such as methyl, ethyl and propyl; aryl, such as phenyl, tolyl and xylyl; aralkyl, such as benzyl and phenethyl; and haloalkyl such as 3,3,3-trifluoropropyl. Methyl, phenyl, and 3,3,3-trifluoropropyl are also preferred for the non-alkenyl silicon-bonded groups in component (A).

55 Component (B), which is a crosslinker, is a polyorganosiloxane having at least 2 silicon-bonded hydrogen atoms in

each molecule. The molecular structure is a straight-chain, partially branched straight-chain, branched-chain, cyclic, or resin structure, with straight-chain and partially branched straight-chain structures being preferred. The silicon-bonded groups in component (B), other than hydrogen, are hydroxyl; alkoxy, such as methoxy, ethoxy and propoxy; and by substituted or unsubstituted monovalent hydrocarbon groups, as described in connection with component (A). Methyl, phenyl, and 3,3,3-trifluoropropyl are also preferred for the non-hydrogen silicon-bonded groups in component (B).

5 Component (B) is added in a quantity that provides from 0.1 to 10 moles, and preferably from 0.5 to 2.0 moles, of silicon-bonded hydrogen from component (B) per one mole total of alkenyl in the silicone rubber composition; that is, per one mole of the total alkenyl present in components (A) and (C). A satisfactory cure will not develop when the addition of component (B) provides less than 0.1 mole or more than 10 moles of silicon-bonded hydrogen from (B) per one  
10 mole of alkenyl in the silicone rubber composition.

Component (C) imparts a soft feel and an excellent hydrophilicity to our silicone rubber powders prepared by our  
15 cure of the silicone rubber composition.

In a first embodiment, component (C) (i) is a polyorganosiloxane that is free of silicon-bonded alkenyl and silicon-bonded hydrogen which contains the polyoxyalkylene group with the formula

15



bonded to silicon, wherein  $R^1$ ,  $R^2$ ,  $R^3$  and  $m$  are as defined above. The other silicon-bonded groups in this embodiment are hydroxyl; alkoxy groups, such as methoxy, ethoxy, and propoxy; and substituted or unsubstituted monovalent  
20 hydrocarbon groups. The substituted and unsubstituted monovalent hydrocarbon groups are alkyl such as methyl, ethyl and propyl; aryl, such as phenyl, tolyl and xylyl; aralkyl, such as benzyl and phenethyl; and haloalkyl such as 3,3,3-trifluoropropyl. Methyl, phenyl, and 3,3,3-trifluoropropyl are also preferred for the other silicon-bonded groups in this embodiment. The molecular structure (C) (i) is a straight-chain, partially branched straight-chain, branched-chain, cyclic, or resin structure, with straight-chain and partially branched straight-chain structures being preferred. Component (C) (i) of this embodiment is exemplified by polyorganosiloxanes with the following formulas:

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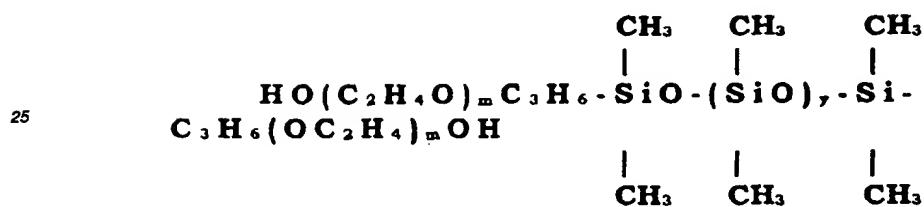
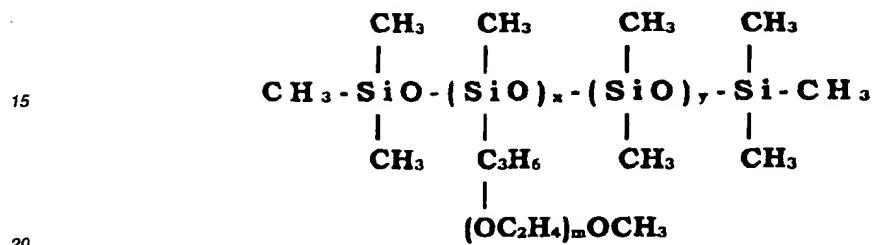
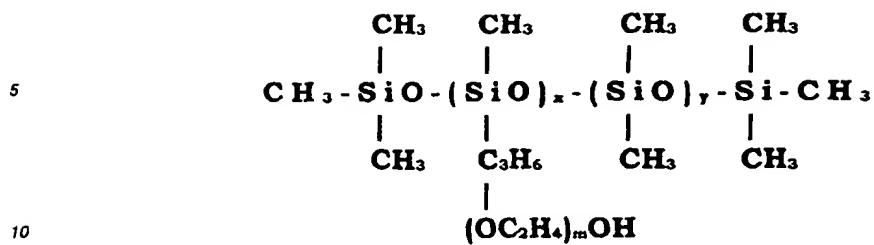
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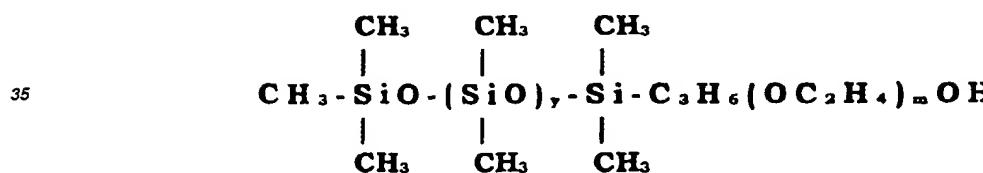
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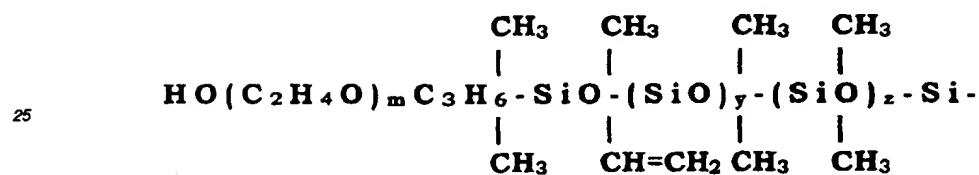
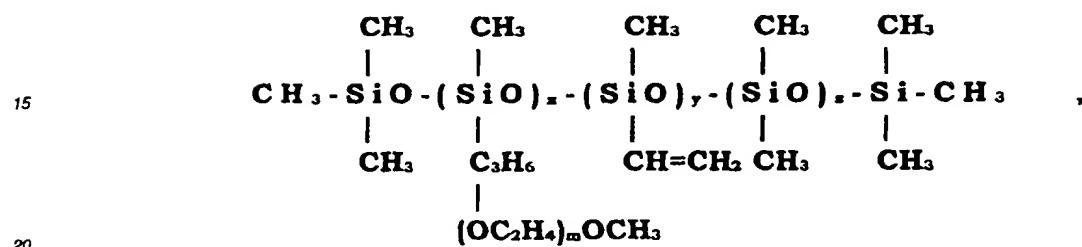
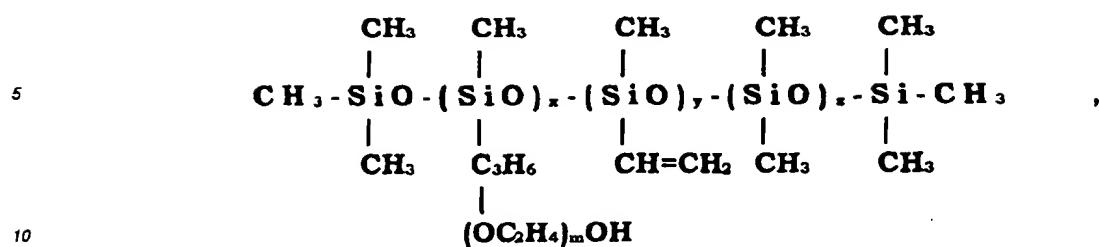
30 and



40 In these formulas, m is an integer with a value of 2 to 100, x is a positive integer, and y is zero or a positive integer.  
 In a second embodiment, component (C) (i) is a polyorganosiloxane that contains silicon-bonded alkenyl or silicon-bonded hydrogen that also contains the polyoxyalkylene group with the formula



bonded to silicon, wherein  $R^1$ ,  $R^2$ ,  $R^3$  and m are as defined above. The alkenyl in this second embodiment is either vinyl, allyl, butenyl, pentenyl, and hexenyl, with vinyl being specifically preferred. The other silicon-bonded groups in this embodiment are hydroxyl; alkoxy, such as methoxy, ethoxy and propoxy; and substituted or unsubstituted monovalent 50 hydrocarbon groups as described in connection with component (A). Component (C) (i) of this second embodiment is exemplified by polyorganosiloxanes with the following general formulas:



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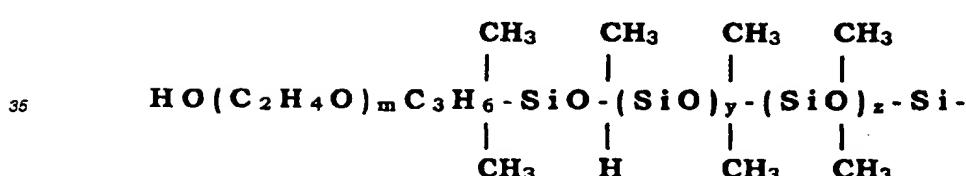
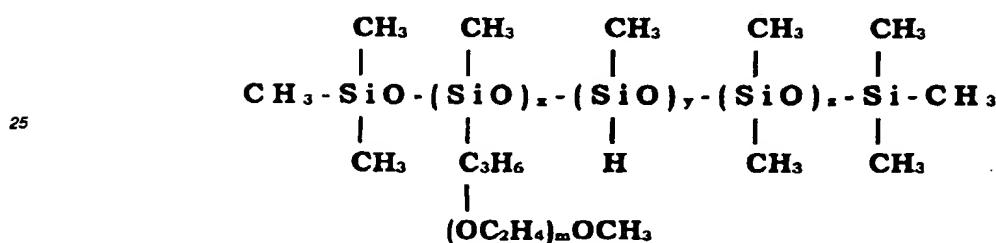
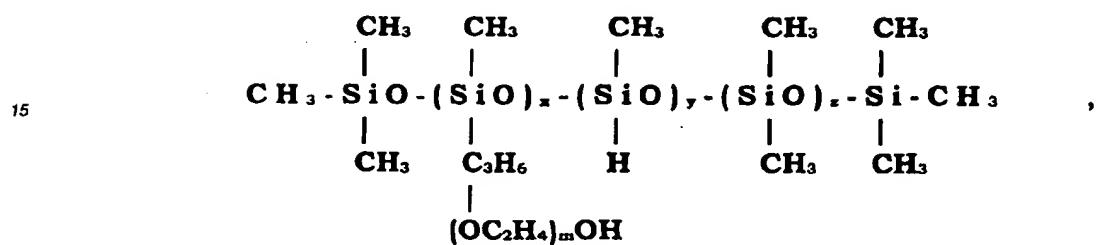
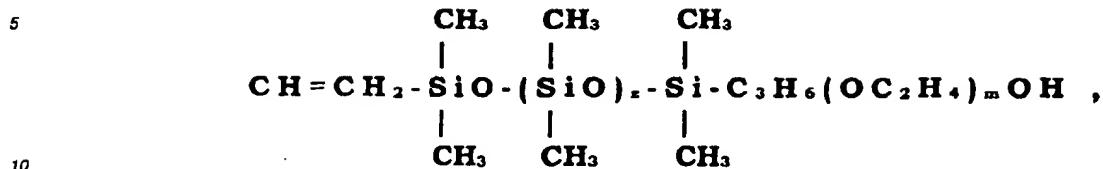
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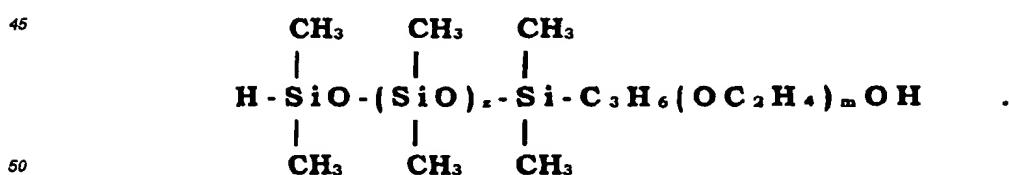
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$C_3H_6(OCH_2CH_4)_mOH$ ,

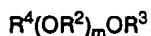


$C_3H_6(OCH_2CH_4)_mOH$  and



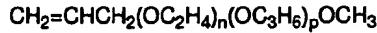
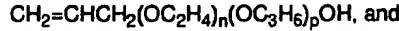
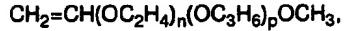
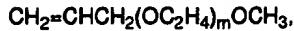
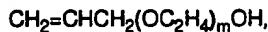
In these formulas, m is an integer with a value of 2 to 100, x is a positive integer, y is a positive integer, and z is zero or a positive integer.

55 Component (C) (ii) is a polyoxyalkylene compound with the general formula



in which  $R^2$ ,  $R^3$ , and m are as defined above.  $R^4$  is an alkenyl radical having 2 to 20 carbon atoms and is selected from

by vinyl, allyl, butenyl, pentenyl, and hexenyl. Component (C) (ii) is exemplified by polyoxyalkylene compounds of the following general formulas:



20 in which m is an integer with a value of 2 to 100, n is zero or a positive integer, p is a positive integer, and (n + p) is an integer with a value of 2 to 100.

Component (C) is added from 0.001 to 20 weight parts per 100 weight parts of component (A). A satisfactory hydrophilicity is not imparted to the silicone rubber powder when component (C) is added at less than 0.001 weight part per 100 weight parts of component (A). The addition of more than 20 weight parts of component (C) per 100 weight parts of component (A) will cause the silicone rubber powder to become tacky or sticky. When component (C) (i) of the second embodiment is used, it is preferably added at from 0.01 to 20 weight parts per 100 weight parts of component (A). When component (C) (ii) is used, it is preferably added at from 0.001 to 10 weight parts per 100 weight parts of component (A).

30 The platinum catalyst (D) is a catalyst for the cure of our curable silicone rubber composition and is exemplified by chloroplatinic acid, alcohol solutions of chloroplatinic acid, olefin complexes of platinum, platinum/alkenylsiloxane complexes, platinum-on-silica powders, platinum-on-active carbon powders, and platinum black.

Component (D) is added in a quantity sufficient to cure the silicone rubber composition. For example, it is preferably added in a quantity that provides 0.1 to 1,000 weight-ppm (parts per million), and more preferably 1 to 500 weight-ppm, of platinum metal in component (D) based on the total weight of components (A) and (B).

35 As optional components, the subject silicone rubber composition contains, for example, inorganic filler such as fumed silica, precipitated silica, quartz powder, fused silica, titanium dioxide, talc, mica, and carbon black. These inorganic fillers may also be used after surface treatment with an organosilicon compound such as organoalkoxysilane, organochlorosilane and organosilazane; Other optional components are addition-reaction inhibitors, such as alkyne alcohols (e.g., 3-methyl-1-butyn-3-ol, 3,5-dimethyl-1-hexyn-3-ol, and phenylbutynol), ene-yne compounds (e.g., 3-40 methyl-3-penten-1-yne or 3,5-dimethyl-3-hexen-1-yne, 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane and 1,3,5,7-tetramethyl-1,3,5,7-tetrahexenylycyclotetrasiloxane, benzotriazole; preservatives; antimicrobials; antioxidants; fragrances; pigments; and dyes.

45 At least 1 inorganic filler selected from talc, mica, and fused silica is preferably added to adjust the specific gravity of our silicone rubber powder. The specific gravity of our silicone rubber powder is preferably from 0.97 to 1.20, and more preferably from 0.97 to 1.10. As a consequence, these inorganic fillers are preferably added at less than 100 weight parts, and more preferably at from 0.01 to 20 weight parts, in each case per 100 weight parts of component (A). Addition-reaction inhibitors are also preferably admixed to improve the handling characteristics of our curable silicone rubber composition. The addition-reaction inhibitor is preferably added at from 10 to 50,000 weight-ppm into the silicone rubber composition.

50 Our silicone rubber powder is highly hydrophilic and has a soft feel. As a consequence, it is useful as a scrub agent in cleansing facial cosmetics, and in waterborne paints, cosmetics, cleaners lustrants.

#### Examples

55 The claimed silicone rubber powder and its method of preparation are explained in greater detail by working examples. The viscosity values reported in therein were measured at 25°C. The silicone rubber powder, its hydrophilicity, and its feel were evaluated as follows.

The average particle size was determined from the weights of silicone rubber powder passing through a series of sieves having different apertures.

Maximum particle size of the silicone rubber powder was determined by inspection on an electron micrograph.

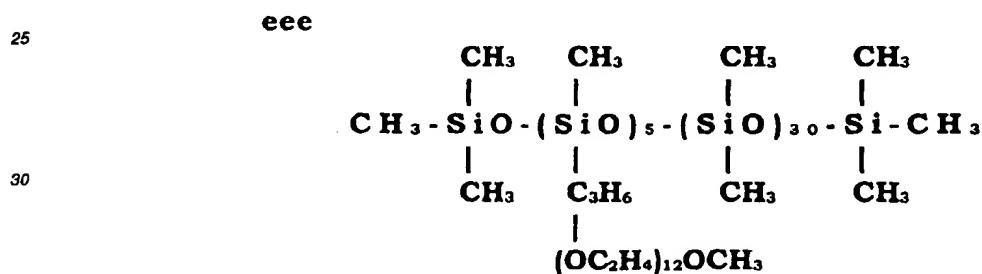
Particle size analysis of the silicone rubber powder was determined by the content (weight%) of silicone rubber powder with a particle size from 50 micrometers to 250 micrometers.

Hydrophilicity of the silicone rubber powder was determined as follows. A waterborne dispersion was prepared from 100 weight parts of the silicone rubber powder, 4 weight parts of polyoxyethylene nonylphenyl ether (HLB = 13.1), and 1,000 weight parts of ion-exchanged water. The waterborne dispersion was then held at quiescence at room temperature for 1 week, after which its status was inspected. A score of "good" was given when the silicone rubber powder did not aggregate in the waterborne dispersion and was easily redispersible. A score of "poor" was given when the silicone rubber powder had aggregated in the waterborne dispersion and could not be redispersible.

10 The above-described waterborne dispersion was applied on the hands to determine "feel". A score of "++" was rendered when the silicone rubber powder had a soft feel. A score of "+" was given when the powder occasionally had an uncomfortable, unnatural feel. A score of "x" was reported when the powder had an uncomfortable, unnatural feel and felt strongly irritating.

15 Example 1

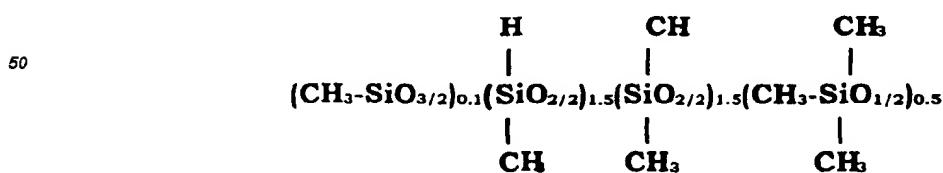
The following were mixed to homogeneity to give an addition-reaction curing silicone rubber composition: 100 weight parts of dimethylvinylsiloxy-endblocked polydimethylsiloxane with a viscosity of 100 mm<sup>2</sup>/s (centistokes), a trimethylsiloxy-endblocked polymethylhydrogensiloxane in a quantity that provided 0.85 mole of silicon-bonded hydrogen per one mole of vinyl in the dimethylvinylsiloxy-endblocked polydimethylsiloxane, an isopropanolic chloroplatinic acid solution in a quantity that provided 5 weight-ppm of platinum metal based on the combined quantity of the preceding siloxanes, one weight part of a polyoxyethylene-functional polymethylsiloxane with the formula



35 and 10 weight parts of a polymethylhydrogensiloxane-treated mica with an average particle size of 4 micrometers. Silicone rubber was prepared by heating this silicone rubber composition at 150°C for 30 minutes. The durometer (JIS A) and specific gravity were measured, and the silicone rubber was then pulverized using a hammer mill having a rotation radius of 20 cm to give a silicone rubber powder. The properties of the produced silicone rubber powder are 40 reported in Table 1.

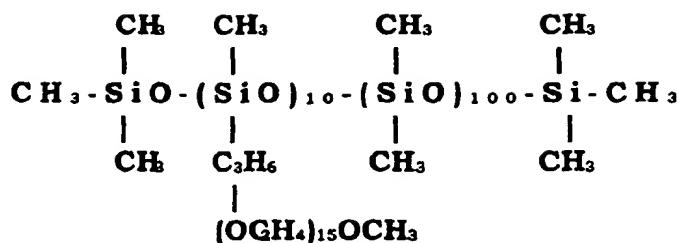
Example 2

The following were mixed to homogeneity to also give an addition-reaction curing silicone rubber composition: 100 weight parts of dimethylvinylsiloxy-endblocked polydimethylsiloxane with a viscosity of 500 mm<sup>2</sup>/s (centistokes), a polymethylsiloxane with the average unit formula



in a quantity that provided 0.95 mole of silicon-bonded hydrogen per one mole of vinyl in the dimethylvinylsiloxy-end-blocked polydimethylsiloxane, an isopropanolic chloroplatinic acid solution in a quantity that provided 10 weight-ppm of platinum metal based on the combined quantity of the preceding siloxanes, 0.5 weight part of a polyoxyethylene-func-

tional polymethylsiloxane with the formula

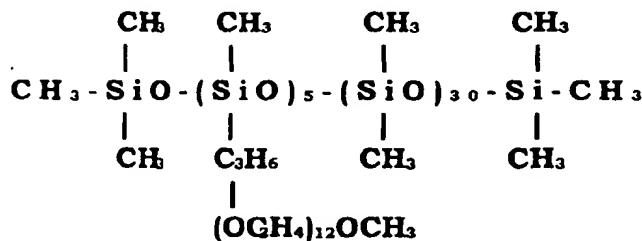


and 14 weight parts of a polymethylhydrogensiloxane-treated talc with an average particle size of 0.5 micrometer.

Silicone rubber was cured by heating this silicone rubber composition at 150°C for 30 minutes. The durometer and specific gravity were measured, and the rubber was then pulverized, as described in Example 1. The properties of this silicone rubber powder product are also reported in Table 1.

Example 3

The following were mixed to homogeneity to also give an addition-reaction curing silicone rubber composition: 100 weight parts of dimethylvinylsiloxy-endblocked polydimethylsiloxane with a viscosity of 500 mm<sup>2</sup>/s (centistokes), a trimethylsiloxy-endblocked polymethylhydrogensiloxane in a quantity that provided 1.2 moles of silicon-bonded hydrogen per one mole of vinyl in the dimethylvinylsiloxy-endblocked polydimethylsiloxane, an isopropanolic chloroplatinic acid solution in a quantity that provided 5 weight-ppm of platinum metal based on the combined quantity of the preceding siloxanes, one weight part of a polyoxyethylene-functional polymethylsiloxane with the formula

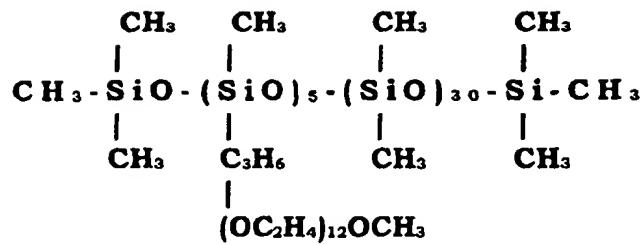


and 10 weight parts of a polymethylhydrogensiloxane-treated mica with an average particle size of 4 micrometers.

The silicone rubber was molded, tested and then pulverized, as described in Example 1. The properties of this silicone rubber powder are also given in Table 1.

Example 4

The following were mixed to homogeneity to give an addition-reaction curing silicone rubber composition: 100 weight parts of dimethylvinylsiloxy-endblocked polydimethylsiloxane with a viscosity of 100 mm<sup>2</sup>/s (centistokes), a trimethylsiloxy-endblocked polymethylhydrogensiloxane in a quantity that provided 0.85 mole of silicon-bonded hydrogen per one mole of vinyl in the dimethylvinylsiloxy-endblocked polydimethylsiloxane, an isopropanolic chloroplatinic acid solution in a quantity that provided 10 weight-ppm of platinum metal based on the combined quantity of the preceding siloxanes, one weight part of a polyoxyethylene-functional polymethylsiloxane with the formula



and 10 weight parts of a polymethylhydrogensiloxane-treated fused silica with an average particle size of 5 micrometers.

15     Silicone rubber was produced, tested and then pulverized as described in Example 1. The properties of the silicone rubber powder are listed in Table 1.

Comparative Example 1

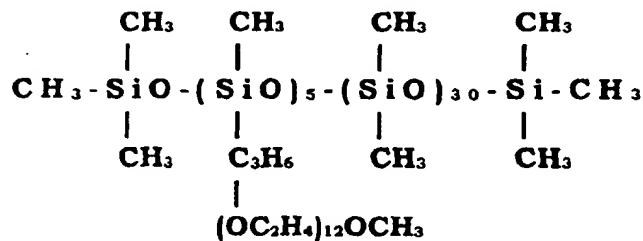
20     The following were mixed to homogeneity to give an addition-reaction curing silicone rubber composition: 100 weight parts of dimethylvinylsiloxy-endblocked polydimethylsiloxane with a viscosity of 100 mm<sup>2</sup>/s (centistokes), trimethylsiloxy-endblocked polymethylhydrogensiloxane in a quantity that provided 1.20 moles of silicon-bonded hydrogen per one mole of vinyl in the dimethylvinylsiloxy-endblocked polydimethylsiloxane, an isopropanolic chloroplatinic acid solution in a quantity that provided 5 weight-ppm of platinum metal based on the combined quantity of the preceding siloxanes, and 10 weight parts of a polymethylhydrogensiloxane-treated mica with an average particle size of 4 micrometers.

This silicone rubber was cured, tested and then pulverized by the method of Example 1. The properties of this silicone rubber powder are also reported in Table 1.

30     Comparative Example 2

The following were mixed to homogeneity to give an addition-reaction curing silicone rubber composition: 100 weight parts of dimethylvinylsiloxy-endblocked polydimethylsiloxane with a viscosity of 100 mm<sup>2</sup>/s (centistokes), a trimethylsiloxy-endblocked polymethylhydrogensiloxane in a quantity that provided 1.20 moles of silicon-bonded hydrogen per one mole of vinyl in the dimethylvinylsiloxy-endblocked polydimethylsiloxane, an isopropanolic chloroplatinic acid solution in a quantity that provided 5 weight-ppm of platinum metal based on the combined quantity of the preceding siloxanes, and 10 weight parts of a polymethylhydrogensiloxane-treated mica with an average particle size of 4 micrometers.

35     This composition was rapidly mixed into 200 weight parts of pure water (electrical conductivity = 0.2 microS/cm) at 25°C and 4 weight parts of a polyoxyethylene-functional polymethylsiloxane with the following formula:



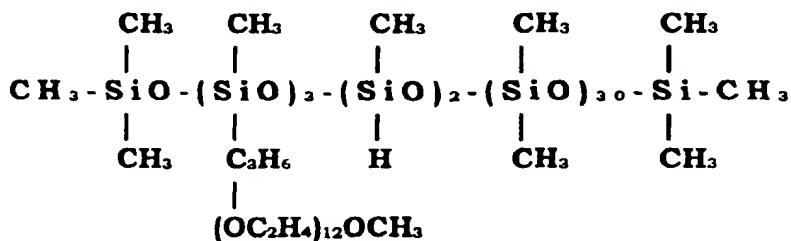
A homogeneous waterborne emulsion of the addition-reaction curing silicone rubber composition was then prepared using an homogenizer (300 kgf/cm<sup>2</sup>). This waterborne emulsion was held for 6 hours at 30°C to give a waterborne dispersion of silicone rubber powder. This waterborne dispersion was heated at 80°C for one hour. However, only a large amount of a gel-like material was produced. After this gel-like material was filtered off with a sieve of 150 mesh (0.105 mm opening), a silicone rubber powder was prepared by drying through a spray drier. The properties of the silicone rubber powder are also given in Table 1.

Table 1

	present invention				comparative examples	
	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Comp. Ex. 1	Comp. Ex. 2
properties of the silicone rubber powders						
JIS A durometer	32	40	34	36	53	53
specific gravity	1.04	1.03	1.02	1.05	1.03	1.03
average particle size (micrometers)	74	74	74	74	53	12
maximum particle size (micrometers)	180	210	150	180	100	200
particle size analysis (%)	92	95	88	86	42	8
hydrophilicity of the silicone rubber powders	good	good	good	good	poor	poor
feel of the silicone rubber powders	++	++	++	++	+	x

Example 5

The following were mixed to homogeneity to give an addition-reaction curing silicone rubber composition: 100 weight parts of a dimethylvinylsiloxy-endblocked polydimethylsiloxane with a viscosity of 100 mm<sup>2</sup>/s (centistokes), a trimethylsiloxy-endblocked polymethylhydrogensiloxane in a quantity that provided 0.85 mole of silicon-bonded hydrogen per one mole of vinyl in the composition, an isopropanolic chloroplatinic acid solution in a quantity that provided 5 weight-ppm of platinum metal based on the combined quantity of the preceding siloxanes, 4 weight parts of a polyoxethylene-functional polymethylsiloxane with the formula

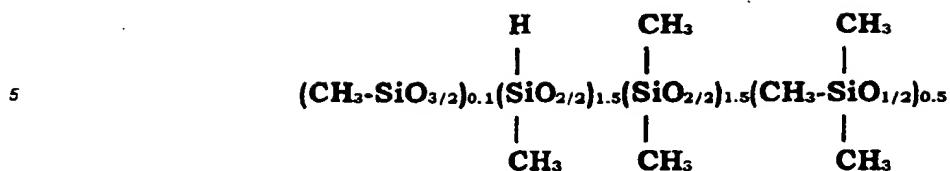


and 10 weight parts of a polymethylhydrogensiloxane-treated mica with an average particle size of 4 micrometers.

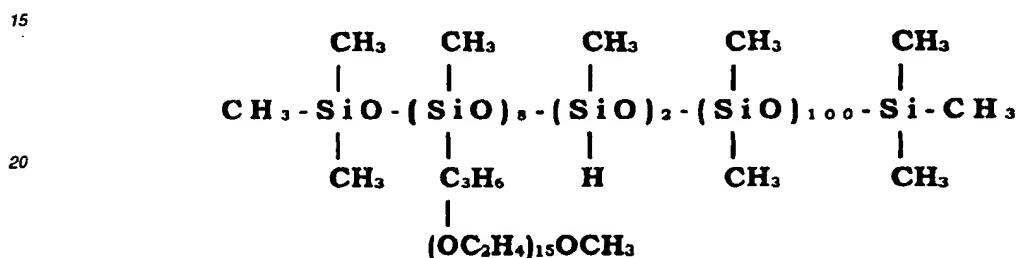
Silicone rubber was prepared, tested and then pulverized, as in Example 1. The properties of this silicone rubber powder are reported in Table 2.

Example 6

The following were mixed to homogeneity to give an addition-reaction curing silicone rubber composition: 100 weight parts of a dimethylvinylsiloxy-endblocked polydimethylsiloxane with a viscosity of 500 mm<sup>2</sup>/s (centistokes), a polymethylsiloxane with the average unit formula



10 in a quantity that provided 0.95 mole of silicon-bonded hydrogen per one mole of vinyl in the composition, an isopropanolic chloroplatinic acid solution in a quantity that provided 10 weight-ppm of platinum metal based on the combined quantity of the preceding siloxanes, 0.5 weight part of a polyoxyethylene-functional polymethylsiloxane with the formula



25 and 14 weight parts of a polymethylhydrogensiloxane-treated talc with an average particle size of 0.5 micrometer.

This silicone rubber was molded, tested and then pulverized, as in Example 1. The properties of this silicone rubber powder are given in Table 2.

30 Example 7

The following were mixed to homogeneity to give an addition-reaction curing silicone rubber composition: 100 weight parts of a dimethylvinylsiloxyl-endblocked polydimethylsiloxane with a viscosity of 100 mm 2/s (centistokes), one weight part of a polyoxyethylene compound with the formula



a trimethylsiloxyl-endblocked polymethylhydrogensiloxane in a quantity that provided 0.90 mole of silicon-bonded hydrogen per one mole of the total amount of vinyl and allyl in the composition, an isopropanolic chloroplatinic acid solution 40 in a quantity that provided 5 weight-ppm of platinum metal based on the combined quantity of the preceding siloxanes, and 10 weight parts of a polymethylhydrogensiloxane-treated mica with an average particle size of 4 micrometers.

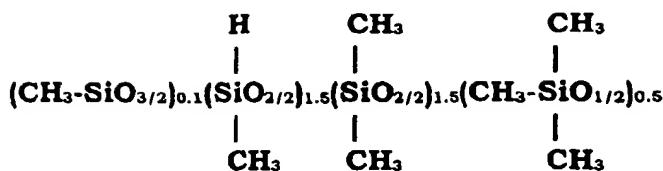
Silicone rubber was cured, tested and then pulverized, as described in Example 1. The properties of the silicone rubber powder are also reported in Table 2.

45 Example 8

The following were mixed to homogeneity to give an addition-reaction curing silicone rubber composition: 100 weight parts of a dimethylvinylsiloxyl-endblocked polydimethylsiloxane with a viscosity of 500 mm 2/s (centistokes), 0.2 weight part of a polyoxyethylene compound with the formula



a polymethylsiloxane with the average unit formula

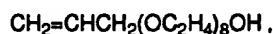


10 in a quantity that provided one mole of silicon-bonded hydrogen per one mole of the total amount of vinyl and allyl in the composition, an isopropanolic chloroplatinic acid solution in a quantity that provided 10 weight-ppm of platinum metal based on the combined quantity of the preceding siloxanes, and 14 weight parts of a polymethylhydrogensiloxane-treated talc with an average particle size of 0.5 micrometer.

15 The silicone rubber was molded, tested and then pulverized, as described in Example 1. The properties obtained are also given in Table 2.

Example 9

20 The following were mixed to homogeneity to give an addition-reaction curing silicone rubber composition: 100 weight parts of a dimethylvinylsiloxy-endblocked polydimethylsiloxane with a viscosity of 500 mm 2/s (centistokes), one weight part of a polyoxyethylene compound with the formula

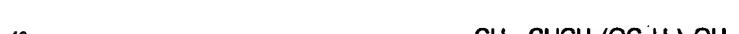


25 a trimethylsiloxy-endblocked polymethylhydrogensiloxane in a quantity that provided 1.30 moles of silicon-bonded hydrogen per one mole of the total amount of vinyl and allyl in the composition, an isopropanolic chloroplatinic acid solution in a quantity that provided 5 weight-ppm of platinum metal based on the combined quantity of the preceding siloxanes, and 10 weight parts of a polymethylhydrogensiloxane-treated mica with an average particle size of 4 micrometers.

30 Silicone rubber was produced, tested and then pulverized, as described in Example 1. The properties of this product are also reported in Table 2.

Example 10

35 The following were mixed to homogeneity to give an addition-reaction curing silicone rubber composition: 100 weight parts of a dimethylvinylsiloxy-endblocked polydimethylsiloxane with a viscosity of 100 mm 2/s (centistokes), one weight part of a polyoxyethylene compound with the formula



a trimethylsiloxy-endblocked polymethylhydrogensiloxane in a quantity that provided 0.90 mole of silicon-bonded hydrogen per one mole of the total amount of vinyl and allyl in the composition, an isopropanolic chloroplatinic acid solution in a quantity that provided 5 weight-ppm of platinum metal based on the combined quantity of the preceding siloxanes, and 10 weight parts of a polymethylhydrogensiloxane-treated fused silica with an average particle size of 5 micrometers.

45 This silicone rubber was molded, tested and then pulverized, as described in Example 1. The properties of the silicone rubber powder are listed in Table 2.

50 Comparative Example 3

The following were mixed to homogeneity to give an addition-reaction curing silicone rubber composition: 100 weight parts of a dimethylvinylsiloxy-endblocked polydimethylsiloxane with a viscosity of 100 mm 2/s (centistokes), a trimethylsiloxy-endblocked polymethylhydrogensiloxane in a quantity that provided 1.20 moles of silicon-bonded hydrogen per one mole of vinyl in the dimethylvinylsiloxy-endblocked polydimethylsiloxane, an isopropanolic chloroplatinic acid solution in a quantity that provided 5 weight-ppm of platinum metal based on the combined quantity of the preceding siloxanes, and 10 weight parts of a polymethylhydrogensiloxane-treated mica with an average particle size of 4 micrometers. This composition was rapidly mixed into 200 weight parts of pure water (electrical conductivity = 0.2 microS/cm) at 25°C and 4 weight parts of a polyoxyethylene nonylphenyl ether (HLB = 13.1). A homogeneous waterborne

emulsion of this silicone rubber composition was then prepared using an homogenizer (300 kgf/cm<sup>2</sup>). This waterborne emulsion was held for 6 hours at 30°C to give a waterborne dispersion of silicone rubber powder. This waterborne dispersion was heated at 80°C for 1 hour and then dried through a spray dryer to give a product silicone rubber powder. The properties of this silicone rubber powder are also reported in Table 2.

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Table 2

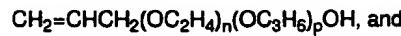
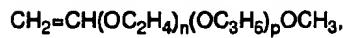
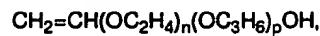
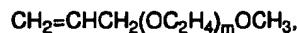
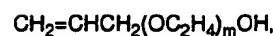
	present invention					comparative examples		
	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9	Ex. 10	Comp. Ex. 1	Comp. Ex. 3
10	properties of the silicone rubber powders							
15	JIS A durometer	32	40	31	41	37	35	53
20	specific gravity	1.04	1.03	1.04	1.03	1.02	1.05	1.03
25	average particle size (micrometers)	74	74	74	74	74	74	53
30	maximum particle size (micrometers)	180	210	180	210	150	180	150
35	particle size analysis (%)	92	95	91	96	89	88	42
40	hydrophilicity of the silicone rubber powders	good	good	good	good	good	good	poor
45	feel of the silicone rubber powders	++	++	++	++	++	+	+

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### Claims

1. A method for preparing a silicone rubber powder, said method comprising:
  - (i) curing a curable silicone composition comprising a polyorganosiloxane which contains at least one silicon-bonded polyoxyalkylene group of the formula
 
$$-R^1(OR^2)_mOR^3$$
 wherein R<sup>1</sup> is an alkylene radical having 1 to 20 carbon atoms, R<sup>2</sup> is an alkylene radical having 1 to 20 carbon atoms, R<sup>3</sup> is selected from hydrogen atom or alkyl radicals having 1 to 10 carbon atoms and m is an integer having a value of 2 to 100 to provide a cured silicone rubber; and
  - (ii) pulverizing said cured silicone rubber.
2. The method of Claim 1, wherein said curable silicone composition further comprises an inorganic filler selected from the group consisting of talc, mica, fused silica and combinations thereof.
3. The method of Claims 1 or 2, wherein said oxyalkylene group comprises repeat units selected from the group consisting of ethylene oxide, propylene oxide and combinations thereof.
4. The method according to Claim 3, wherein said polyorganosiloxane is polydimethylsiloxane.
5. The method according to Claim 3, wherein R<sup>1</sup> is selected from ethylene or propylene, and R<sup>3</sup> is selected from the group consisting of hydrogen atom or methyl, ethyl and propyl.
6. The method according to Claim 3, wherein said polyorganosiloxane is a polyoxyalkylene-containing component having a formula selected from the group consisting of
 
$$CH_2=CH(OC_2H_4)_mOH,$$

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15 in which m is an integer with a value of 2 to 100, n is zero or a positive integer, p is a positive integer, and (n + p) is an integer having a value of 2 to 100.

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(19)

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(11)

EP 0 796 883 A3

(12)

EUROPEAN PATENT APPLICATION

(88) Date of publication A3:  
22.04.1998 Bulletin 1998/17

(51) Int. Cl.<sup>6</sup>: C08J 3/12, C08J 3/24,  
C08L 83/12

(43) Date of publication A2:  
24.09.1997 Bulletin 1997/39

(21) Application number: 97104878.0

(22) Date of filing: 21.03.1997

(84) Designated Contracting States:  
DE FR GB IT

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(30) Priority: 22.03.1996 JP 93287/96  
22.03.1996 JP 93288/96

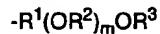
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(54) Silicone rubber powder and preparation thereof

(57) There is disclosed a silicone rubber powder prepared from a curable silicone composition comprising a polyorganosiloxane having least one silicon-bonded polyoxyalkylene group of the formula



wherein R<sup>1</sup> is an alkylene radical, R<sup>2</sup> is an alkylene radical, R<sup>3</sup> is selected from hydrogen atom or alkyl radicals and m is an integer having a value of 2 to 100. The product rubber powder is preferably prepared by curing the above curable silicone composition to form a cured silicone rubber and by then pulverizing the product silicone rubber.

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European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number

EP 97 10 4878

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.6)						
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim							
X	EP 0 309 722 A (TORAY) * page 8, line 18 - line 23 * ---	1-6	C08J3/12 C08J3/24 C08L83/12						
A	FR 2 630 125 A (TOSHIBA) * page 5, line 13 - line 19 * ---	1							
A	EP 0 545 002 A (KOSE CORP) * page 2, line 20 - line 21 * * page 2, line 43 - line 44 * ---	1							
A	EP 0 131 446 A (TORAY) * claim 1 * -----	1							
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)						
			C08J C08L						
<p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 33%;">Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>23 February 1998</td> <td>Lentz, J</td> </tr> </table>				Place of search	Date of completion of the search	Examiner	THE HAGUE	23 February 1998	Lentz, J
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CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document							
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